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CRITICAL BEHAVIOUR OF COPOLYMER : SOME EXACT RESULTS ON FRACTAL LATTICE

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Abstract : We study the critical behaviour of copolymer on 4-simplex lattice. We show that in absence of inter-chain interaction co-polymer behaves as a single polymer chain, however, due to inter-chain interaction the critical behaviour of co-polymer changes.

Keywords : Copolymer, Renormalization Group Theory, Fractal

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Di-block co-polymers are polymers formed by two blocks of monomers of different chemical nature **A** and **B** linked together. From the theoretical side, block co-polymers can be studied using the statistical methods developed for homopolymer [1-3]. In our recent papers [4-6] we developed a model of two interacting walks (TIWs) on fractal lattices to study the behaviour of two chemically different linear polymers in selective solvent. Depending on the solvent quality and attractive interaction between inter-chain and intra-chain monomers, many different situation may arise. We showed that the system will be in either of three states described below [5] :

(1) The system may be in a state in which the two polymers intermingled with each other in such a way that they can not be distinguished from the other chain. This state was referred as the interpenetrated state.

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(2) When the attractive interaction between unlike monomers reaches a critical value, the two chains may be found in the zipped state in such a way that they lie side by side (in some approximate sense is similar to the formation of double stranded DNA). It was referred as a zipped state.

(3) If the quality of the solvent is such that the one or both polymers are in compact globule state, the two chains at high temperature are separated from each other without any overlap, we referred it as segregated state.

In this paper we show that the model of two interacting walks (TIWs) may be extended to study the critical behaviour of copolymers in a solution which may have different qualities for different chains. Here we apply real-space-renormalization group technique [7] to study this problem. This technique was found to be very useful in case of fractal lattices where the asymptotic properties of the polymer chain are obtained by using exact recursion relations [4-6]. These recursion relations have been obtained by splitting generating functions in finite subsets. The variables in these equations are just the partial generating functions corresponding to different polymer configurations for a given size of the fractal lattice. Linearizing the recursion equation near the fixed points, one can find the eigenvalues of the transformation matrix which give the characteristic exponent of the system. The generating function of our interests can be written as

$$G(P_1P_2x_3u_3) = \sum_{\text{all distinct walks}} (x_1^{N_1}u_1^{R_1})(x_2^{N_2}u_2^{R_2})(x_3^{N_3}u_3^{R_3}) \qquad (1)$$

where $N_1(N_2)$ is the number of monomers in the polymer $P_1(P_2)$ and $x_1(x_2)$ denotes the fugacity weight attached to each step of polymers $P_1(P_2)$. Here $u_1(u_2)$ represents the Boltzmann factor associated with the attractive interaction between monomers of polymer $P_1(P_2)$. x_3 and u_3 denote, respectively, the fugacity weight attached with zipped walks and the Boltzmann factor associated with the attractive interaction between unlike monomers. N_3 is the total number of zipped monomers. $R_1(R_2)$ is the total number of monomers of the chain $P_1(P_2)$ occupying the nearest neighbouring sites of the lattice and R_3 is the number of monomers of different chain occupying the nearest neighbour lattice points.

We take chains P_1 and P_2 in a given configuration, the variables (x_1u_1) and (x_2u_2) are therefore taken to be known [8-9]. From the generating function one can calculate the average number of monomers of two chains in contact with each other and the divergence of generating function determines the end to end distance exponent of copolymer analogous to the single polymer chain [5]. For 4-simplex lattice it is possible to write the relevant generating functions in terms of restricted partition functions shown in Fig. 1.

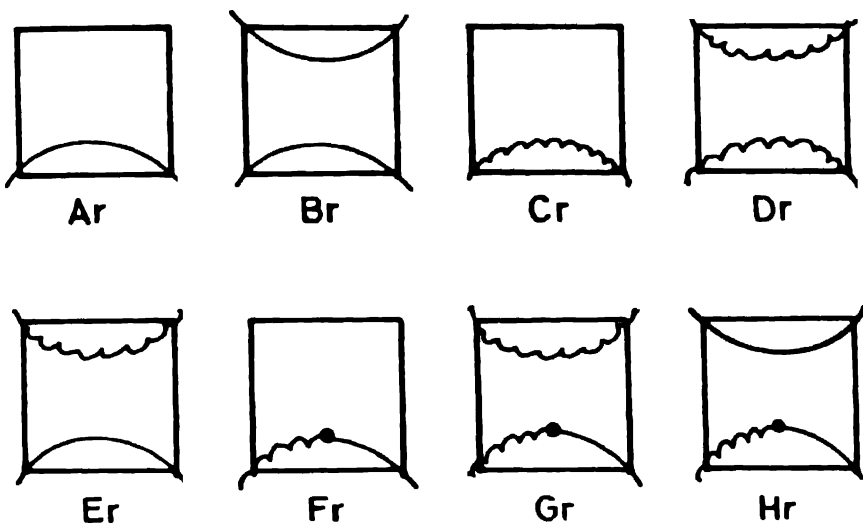

Fig. 1. Diagrams representing the eight restricted partition functions for co-polymers indecated by plane and wigel line on truncated 4 - simplex lattice.

These partition functions are defined recursively as a weighted sum over all possible configurations for a given stage of the iterative construction of fractals. These recursion relations are

$$A_{r+1} = f(A_r, B_r) \quad (2a)$$

$$B_{r+1} = g(A_r, B_r) \quad (2b)$$

$$C_{r+1} = h(C_r, D_r) \quad (2c)$$

$$D_{r+1} = i(C_r, D_r) \quad (2d)$$

$$E_{r+1} = j(A_r B_r, C_r D_r, E_r) \quad (2e)$$

$$F_{r+1} = k(A_r B_r, C_r D_r, E_r F_r, G_r H_r) \quad (2f)$$

$$G_{r+1} = l(A_r B_r C_r D_r E_r F_r G_r H_r) \quad (2g)$$

$$H_{r+1} = m(A_r B_r C_r D_r E_r F_r G_r H_r) \quad (2h)$$

Depending on initial conditions, we may find a polymer chain in either of three states : Swollen (S), Compact globule (C) and at the θ-point (T) [8-9]. The effect of inter-chain interaction between two polymers are taken through E, F, G and H.

In a system of two chemically different polymer chains we have six independent combinations of the individual chains, which we indicate by SS, CC, TT, SC, ST and CT. Using the fixed point (A^*B^*) and (C^*D^*) corresponding to these states of polymers P_1 and P_2 we solve Eqs. (2a-2h), which give two fixed points E_0^* and E_1^* for each combination of the states of the individual chain. Using these values we determine F^*, G^* and H^*. Values of fixed points, relevant eigenvalues, contact exponent and the end to end distance exponent ν for different possibilities are given in Table 1. Fixed points, corresponding eigenvalues $\lambda_1\lambda_2(\lambda_3\lambda_4)$ and λ_6 and other critical exponents may be found from Ref. [5].

Table 1

Values of fixed points, relevant eigenvalues, contact exponent and end to end distance exponent at the tricritical point for the 4-simplex lattice. The swollen, compact globule and tricritical configuration of each chain is indicated by S, C and T respectively.

State of individual chain	Fixed point for the state of composite system	λ_6	λ_7	λ_8	y	End to end distance exponent of composite chain	End to end distance exponent of individual chain
SS	$E_0^* = 0.049$ $E_1^* = 0.612$	2.7965 4.9510	< 1.0 2.6258	< 1.0 = 1.0	0.945	$\nu_0 = 0.433$	0.674
TT	$E_0^* = 0.014$ $E_1^* = 1/3$	1.955 2.222	= 1.0 2.222	< 1.0 3.703	0.603	$\nu_0 = 0.529$	0.529
CC	$E_0^* = 0$ $E_1^* = 0.22^{1/3}$	0 0	= 1.0 4.0	= 1.0 2.544	0.673	$\nu_0 = 0.5$	0.5
ST	$E_0^* = 0.026$ $E_1^* = 0.429$	2.3292 4.2062	= 1.0 = 1	< 1.0 2.8253	0.631	$\nu_0 = 0.482$	0.529
SC	$E_0^* = 0.0$ $E_1^* = 0.488$	= 1 4.8261	= 1.0 = 1	< 1.0 1.5756	0.756	$\nu_0 = 0.440$	0.5
TC	$E_0^* = 0.0$ $E_1^* = 0.368$	0 = 1	< 1.0 2.4715	< 1.0 4.0	0.682	$\nu_0 = 0.5$	0.5

We have studied the critical behaviour of copolymers on fractal lattices. The problem with which we have been concerned here is to predict the effect of inter-chain interaction on end to end distance exponent. In all these cases it is evident from Table.1 that end to end distance exponent is unaltered when the inter-chain interaction is less than the critical value. However, at the critical value of inter-chain interaction the copolymer try to collapse as evidenced by the increase in eigenvalues which show that average density of monomer increases. It may be noted that in all these cases the end to end distance exponent is found to be lower than $\nu = 1/d_f$, where d_f is the fractal dimension of the lattice but greater than the $\nu_R = d_s/2d_f$ [10], where d_s is the spectral dimension of the fractal. ν_R is the end to end distance exponent of random walk on the particular fractal. We have also studied the behaviour of co-polymer when both the chains are not in the same state. In most of the cases reported above we find one of the eigenvalue is equal to 1. In the framework of real space renormalization group calculation this eigenvalue is referred as "marginal eigenvalue" which corresponds that the fixed point is unstable. To get the stable fixed points one has to include 2^{nd} order term in linearization. The detailed phase diagram, relevance of different fixed points in terms of the universality and other features of this model will be published else where.

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